

ATOMISTIC SIMULATIONS OF TI AND CR ALLOYING ADDITIONS TO NiAl USING THE BFS METHOD

Guillermo Bozzolo
Ohio Aerospace Institute
22800 Cedar Point Road
Cleveland, Ohio 44142

Ronald D. Noebe, John Ferrante
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Anita Garg,
AYT Corporation
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

and

Carlos Amador
Facultad de Quimica
Universidad Nacional Autonoma de Mexico, Mexico

SUMMARY

Alloying additions of Ti to NiAl are of technological interest since NiAl-Ti alloys are extremely creep resistant. Also, Cr additions are of interest due to its low solubility and the potential for precipitating α -Cr, which at higher volume fractions acts as a ductile phase toughening component. However, very little is known about the structure of the corresponding ternary alloys besides the formation of Ni-Al-Ti Heusler precipitates or the phase separation of Cr in the NiAl+Cr alloys. Consequently, an atomistic analysis of NiAl+X (X = Ti,Cr) alloys using the method of Bozzolo, Ferrante and Smith (BFS) for alloys, along with complementary TEM analysis, was performed. The results include the determination of the corresponding solubility limits for each alloying addition, site preference and the formation of ordered structures within the B2 NiAl matrix. Analytical results as well as temperature dependent Monte Carlo numerical simulations are presented, highlighting the formation of Ni₂AlTi Heusler precipitates and the α -Cr phase separation, in excellent agreement with experiment.

INTRODUCTION

It is now well recognized that ternary and higher order additions to structural intermetallics are essential for the optimization of physical, chemical and mechanical properties. However, the role of these additions in controlling the properties is poorly understood due to the lack of detailed microstructural information. The general approach to the design of a new alloy is usually empirical in nature, which due to its inherent practical limitations does not provide a complete understanding of the structure-property relationships. As an example, in a NiAl-Ti system, Ti additions of the order of 2.5 to 3.0 at.% have been shown to result in a 200 to 5000 fold reduction in creep rate as compared to that of the binary NiAl (ref. 1). However, from a microscopic point of view, this behavior is not clearly understood, thus limiting our ability to modify and further improve the alloy properties. This creates the need to develop a theoretical modelling approach to alloy design which is capable of predicting microstructural changes as a function of different alloy compositions.

Obtaining accurate quantitative and qualitative theoretical analysis of multicomponent systems is the goal of most current theoretical techniques, generally divided between first-principles and semiempirical methods.

First-principles calculations of simple binary systems have been successful in determining the basic properties of simple binary systems, and recently some work has been published on ternary alloys also (ref. 2). However, the scope of this work is limited both by the increasing complexity of these systems as well as by the extensive computational effort required even for the determination of the most basic properties. Semiempirical techniques have also been applied to the binary and ternary systems, but with a varied degree of success. Also, most of the available techniques impose limitations on the type of elements and the crystallographic structure of the configuration to be studied.

In this work, we apply the BFS (Bozzolo-Ferrante-Smith) method (ref. 3) for a comprehensive study of the effect of Ti and Cr additions to NiAl, exploiting the versatility of the method in dealing with any element and any given crystallographic configuration, a degree of freedom included in the formulation of the method. After a brief description of the BFS method, we concentrate on its application to the study of Ni-Al-Ti and Ni-Al-Cr alloys, their physical properties, resulting defect structures, the solubility of Ti or Cr in NiAl and precipitation of a second phase in both cases. The results also include Monte Carlo temperature-dependent large-scale simulations, providing some insight on the relationship between heat treatment and microstructure. Finally, the theoretical results are successfully compared with the results from a concurrent transmission electron microscopy study. We conclude with a brief discussion of the potential applications of the methodology introduced in this paper.

THE BFS METHOD

The BFS method for alloys aims at the problem of performing large scale computer simulations of complex, multicomponent systems. For a given atomic distribution, the BFS method computes the configurational energy of formation by means of a perturbation theory-based approach. The only input necessary for its parameterization are four parameters for each single element and two for each binary combination. These are generated from first-principles Linear Muffin Tin Orbital (LMTO) full-potential calculations (ref. 4). Ground state structures are obtained by optimizing the atomic distribution via Monte Carlo simulations. Several features distinguish this method from other competing techniques e.g. there are no restrictions on the number and type of elements to be considered, and on the crystallographic structure. For the sake of brevity, we refer the reader to previous papers on the BFS method and its application to alloy design problems (ref. 5).

The BFS method is based on the idea that the energy of formation of an alloy is the superposition of individual contributions ϵ of nonequivalent atoms in the alloy:

$$\epsilon = \epsilon^S + g(\epsilon^C - \epsilon^0) \quad (1)$$

where ϵ^S is the strain energy which is computed with perturbation theory-based Equivalent Crystal Theory (ECT) (ref. 6), that accounts for the actual geometrical distribution of the surrounding atoms, computed as if they were of the same atomic species, and $\epsilon^C - \epsilon^0$ is the chemical energy, which takes into account the different atomic species of each neighboring atom. We represent this defect by 'perturbing' the electron density in the overlap region between dissimilar atoms, and locating them at equilibrium lattice sites of the reference atom is a reference energy that ensures that the chemical energy ϵ^0 is free from any structural information. The coupling function g ensures the correct asymptotic behavior of the chemical energy and it depends on the magnitude of the strain energy: $\epsilon = e^{-a}$, where a is a solution of $\epsilon^S = (-E_C)[1 - (1 + a)e^{-a}]$.

In the context of the BFS method, the terms 'strain' and 'chemical' represent different effects from the usually assigned meanings. Finally, only two parameters referring to alloy properties enter in the formulation of BFS and these are used in the calculation of the chemical energy contribution. These parameters, listed in tables I and II, are obtained from first-principles calculation for each binary pair A-B. The parameters for Ni, Al, Ti and Cr have been taken from previous successful applications of BFS to NiAl based alloys (ref. 7).

RESULTS AND DISCUSSION

The application of the BFS method to the study of NiAl+X (X = Ti,Cr) can be divided into an analytical description of the system and a numerical, Monte Carlo-based study. We first perform a 'static' analysis, where we construct a large set of atomic distributions on a computational cell of a fixed size. These configurations are

amenable to a detailed description via the analytic version of the BFS method and provide insight into the reasons why certain atomic distributions are preferred, leading to the determination of alternative ordering patterns. Based on a 72-atom cell, a few hundred atomic configurations were defined and then their energy computed using the BFS method (ref. 7). The lowest energy configurations amongst the input configurations along with a series of possible metastable structures (configurations with energies close to that of the ground state) are thus obtained. Moreover, the site preference of the alloying element as a function of alloy concentration and information regarding the solubility limit and possible formation of second phases are also obtained. Figure 1 shows some of the simple configurations included as input configurations for the NiAl-X (X = Ti, Cr) system.

Figure 2 displays the calculated energy of formation of the set of input configurations as a function of Ti concentration. Each point corresponds to a certain atomic configuration, characterized by a particular short- or long-range ordering, or no ordering at all. It is clear from figure 2 that the configuration which displays Heusler ordering (Ti atoms occupying Al sites only, separated by next-nearest-neighbor distance) has, above 5 at. % Ti, the lowest energy. Below this concentration, configurations with Ti in solid solution in the NiAl matrix are energetically favored. This information can be taken as an indirect way of determining the solubility limit of Ti (~5 percent) in NiAl. Beyond this value, Heusler precipitates begin to form. The lattice parameter of 0.5828 nm for the Ni₂AlTi phase (from the $x_{Ti} = 25$ calculation) is in excellent agreement with the reported experimental value of 0.5876 nm (ref. 8). Thus, based solely on the BFS calculations, the lattice mismatch between NiAl and Ni₂AlTi is found to be 1.7 percent which is very close to the 1.5 percent misfit obtained experimentally via TEM.

Figures 3 (a) to (c) shows TEM microstructures of the alloys Ni-47Al-3Ti, Ni-45Al-5Ti, and Ni-40Al-10Ti. The microstructure of the Ni-47Al-3Ti alloy (fig. 3(a)) is featureless, suggesting that 3 at. % Ti is in solid solution in the NiAl matrix. However, precipitation of a high density of fine Heusler phase is clearly seen in the 5 percent Ti (fig. 3(b)) and 10 percent Ti (fig. 3(c)) alloys, confirming the predictions of the BFS model.

While the results of figure 2 provide evidence for the formation of a Heusler phase and its stability, further concurrent evidence can be found from the results of temperature-dependent Monte Carlo simulations using the BFS method to calculate the energy at every step. Typical results are shown in figure 4, where the final state of a 1024-atom cell is shown for three NiAl+Ti alloys. The simulations start with a random distribution of atoms at a high temperature. The sample is slowly cooled allowing for maximum ordering. In each step in the simulation, a pair of atoms of different species is exchanged, which is assigned a probability given by $\exp(-\Delta E/kT)$, where k is the Boltzmann constant, T is the temperature and ΔE is the difference in energy of the computational cell before and after the exchange. The results shown in figure 4 indicate that the same features observed experimentally can be seen in these results: Ti atoms in solid solution below 5 percent Ti, indication of Heusler ordering at 5 percent Ti and the formation of Heusler precipitates above that concentration.

The Monte Carlo results are clearly useful in visualizing the atomic behavior of the alloying additions, although the information necessary to understand and predict such behavior can already be found in the analytical results in figure 2. In addition, site preference of alloying elements can also be calculated by the BFS method in the form of an 'energy spectrum', as shown in figure 5. The energy of formation of a set of configurations covering almost every possible site substitution scheme is shown, which helps to visualize the relative probability of each possible defect. From this set, it is seen that Ti preference for Al sites in NiAl dominates. This marked preference scheme explains the ordering patterns seen already at low Ti concentrations, where Ti atoms substitute randomly for Al in NiAl solid solution. At higher Ti concentration (above 5 at. % Ti) Ti atoms tend to locate themselves at opposite corners of the cube in the Al-sublattice, so that they always have Al atoms as second neighbors, indicative of Heusler phase formation. This is seen clearly in the $x_{Ti} = 6.94$ energy spectrum (fig. 5) where Ti atoms show preference for Heusler patterns over Ti atoms in solid solution. In all cases, there is a noticeable energy gap between Ti(Al) and Ti(Ni)Al states.

In the site preference scheme, Cr additions to NiAl behave quite differently. The gap between Cr(Al) and Cr(Ni)Al is not as wide as in the Ti case. Cr(Al) substitutions are favored, but this preference is less pronounced as the Cr concentration increases. The fact that Cr atoms—in large concentration do not show any clear preference for either site hint to the possibility for the formation of a Cr precipitate. BFS calculations in the NiAl-Cr system using similar configuration catalogues as the ones used for NiAl-Ti alloys show that at low Cr concentration (<1 at. % Cr) those configurations with Cr atoms randomly distributed in the NiAl matrix are energetically favorable. Beyond 1 to 2 at. % Cr, the BFS method predicts that a new configuration is favored, where the B2 NiAl matrix phase coexists with a pure α -Cr precipitate. The site preference scheme of Cr in NiAl indicates the tendency for displaced Ni atoms to form an interphase boundary between the NiAl matrix and the α -Cr precipitate in some cases. Experimental results confirm these predictions: Figure 6 shows a TEM micrograph confirming the precipitation of Cr in a

Ni-45Al-5Cr alloy. Moreover, the ternary phase diagram confirms the BFS predictions of the formation of a three-phase alloy in the Ni-25Al-25Cr alloy, as shown in the results of the Monte Carlo simulation displayed in figure 7. Also, figure 7 includes the results of a simulation of a Ni-33Al-34Cr clearly showing the two phase structure of this alloy.

CONCLUSIONS

The BFS method successfully describes the atomic behavior of Ti and Cr alloying additions to NiAl. The results of analytical calculations based on a large number of ideal 'static' states, together with the results of temperature dependent Monte Carlo simulations predict the correct solubility limits for each alloying addition as well as the formation of a second phase in each case. The site preference scheme can be easily computed, for an arbitrary number of site substitution schemes, thus simplifying the interpretation of results obtained from Monte Carlo calculations.

The theoretical results also display excellent agreement with the experimental data, thus raising confidence in the validity of the BFS method and the parameterization used. In principle, these parameters are transferrable and once proven reliable as in the present study, can be used without any further adjustment in any other structural study involving Ni, Al and Ti.

One advantage of the methodology used in this work resides in the lack of restrictions regarding the structural and chemical composition of the system being studied, which may be an insurmountable obstacle for other theoretical techniques of the same nature. It is therefore easy to analyze complex systems in great detail, obtaining fundamental basic information on the phase structure of the alloy. Moreover, the simplicity of the formalism translates into computational efficiency, which makes this type of analysis a helpful tool for the process of alloy design, as it provides immediate answers to some of the fundamental properties of the systems at hand, thus complementing the experimental work which due to inherent constraints could leave some of the fundamental mechanisms unexplained.

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TABLE I.—LMTO AND BFS PARAMETERS USED

LMTO parameters for pure A bcc elements				
A	a_0 , Å	E_c , eV/at	B_0 , GPa	E_v , eV/at
Ni	2.752	5.689	249.2	3.0
Al	3.192	3.945	77.3	1.8
Ti	3.213	6.270	121.0	2.0
Cr	2.837	4.981	286.0	4.9

a_0 —the equilibrium lattice parameter.

E_c —the cohesive energy.

B_0 —the bulk modulus.

E_v —the single vacancy formation energy.

(See ref. 3 for a detailed explanation of their use).

TABLE II.—BFS PARAMETERS (SEE REF. 7)

BFS PARAMETERS FOR B2 A-B ALLOYS					
A-B	$\Delta_{AB}(\text{\AA}^{-1})$	$\Delta_{BA}(\text{\AA}^{-1})$	A-B	$\Delta_{AB}(\text{\AA}^{-1})$	$\Delta_{BA}(\text{\AA}^{-1})$
NiAl	-0.05813	0.08220	AlTi	-0.06360	0.22830
NiTi	-0.06587	0.4610	AlCr	-0.01307	-0.01637
NiCr	0.02975	0.20480	TiCr	0.06579	-0.04691

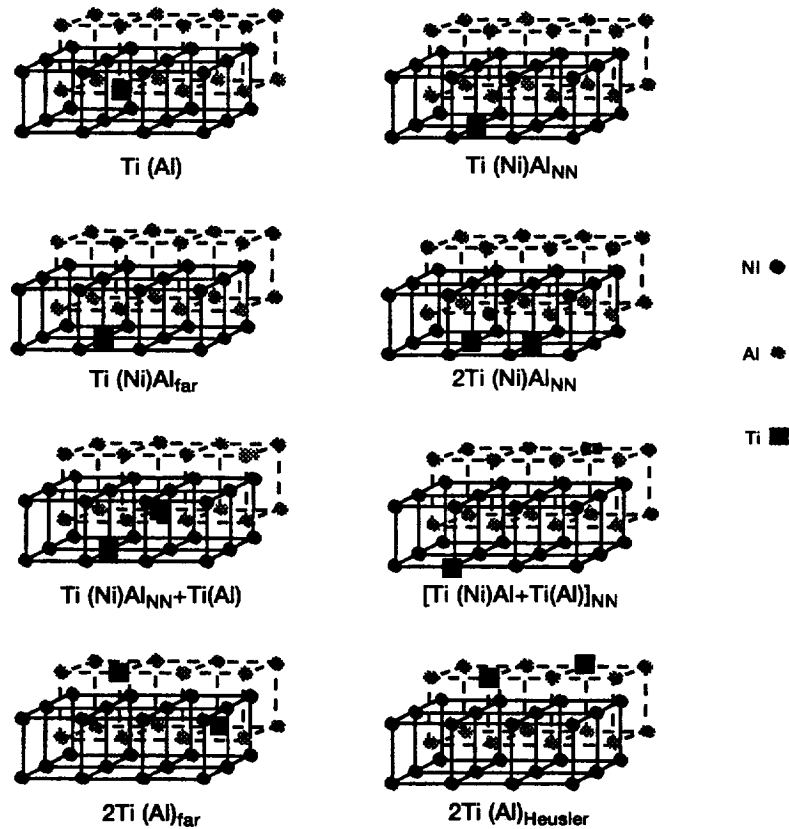


Figure 1.—Computational cells showing different substitutional schemes for Ti in NiAl. The corresponding energies of formation and lattice parameter are shown in Fig. 2. A(B) describes a configuration where an A atom occupies a site in the B-sublattice. A(B)C is the superposition of two substitutional defects: A(B)+(B)C. The subindices NN, far and Heusler indicate that the substitutional atoms are either at nearest-neighbor distance, at distances greater than nearest-neighbor distance or located following Heusler ordering (in opposite corners of the cube in the same sublattice).

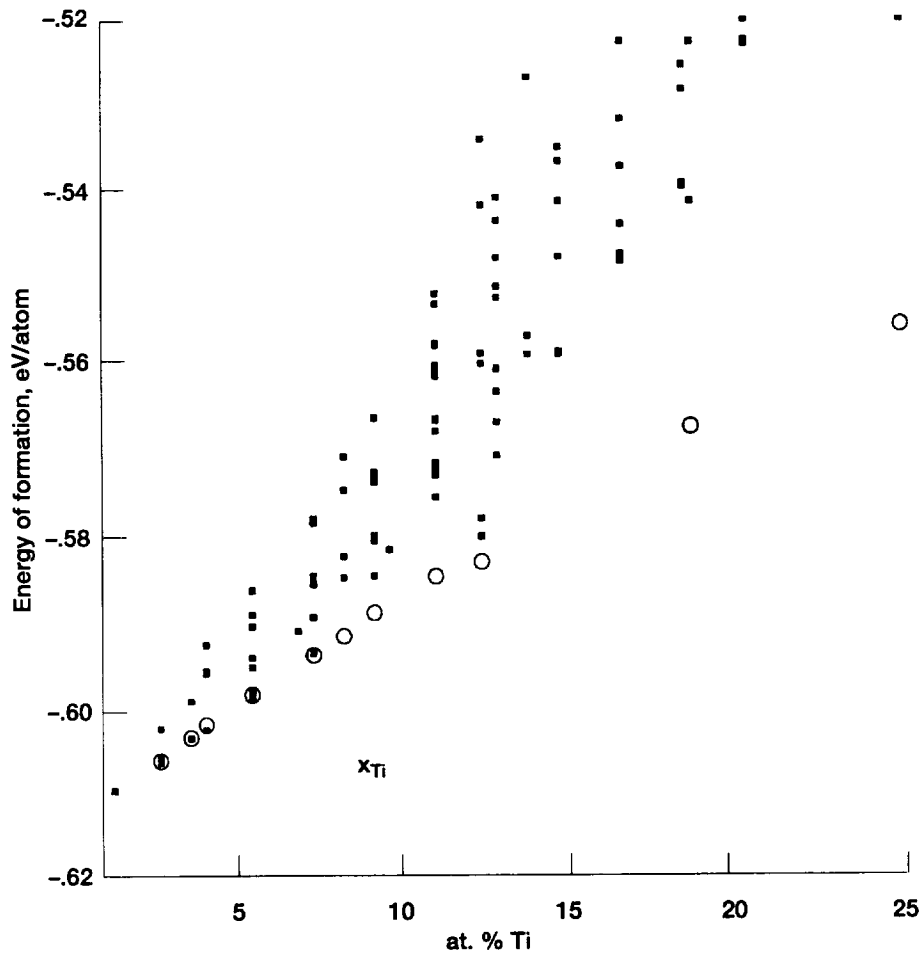


Figure 2.—Energy of information vs. Ti concentration of a large number of $\text{Ni}_{50}(\text{Al}_{50-x}\text{Ti}_x)$ bcc-based configurations (defined in Appendix 2 of Ref. 9), displaying a variety of short-range order patterns as well as completely disordered states. Those configurations characterized by Heusler ordering are denoted with open circles, whereas the solid squares indicate other configurations. For a given Ti concentration, configurations with increasing disorder are higher in energy. Below 5% Ti, the configurations characterized by Ti atoms in solid solution in the NiAl matrix are slightly lower in energy than those where the Ti atoms locate themselves in Al sites following Heusler ordering (where given Ti atom only has Al atoms as next-nearest-neighbors). Beyond 5 % Ti, Heusler-like arrangements are consistently lower in energy than any other option. At 12.5% Ti there is a slight departure from the smooth curve defined by the open circles, due to the higher symmetry configuration where all the existent Ti atoms in the sample have the same coordination. The gap between Heusler configurations and the others increases until it achieves a maximum value at 25 at. % Ti.

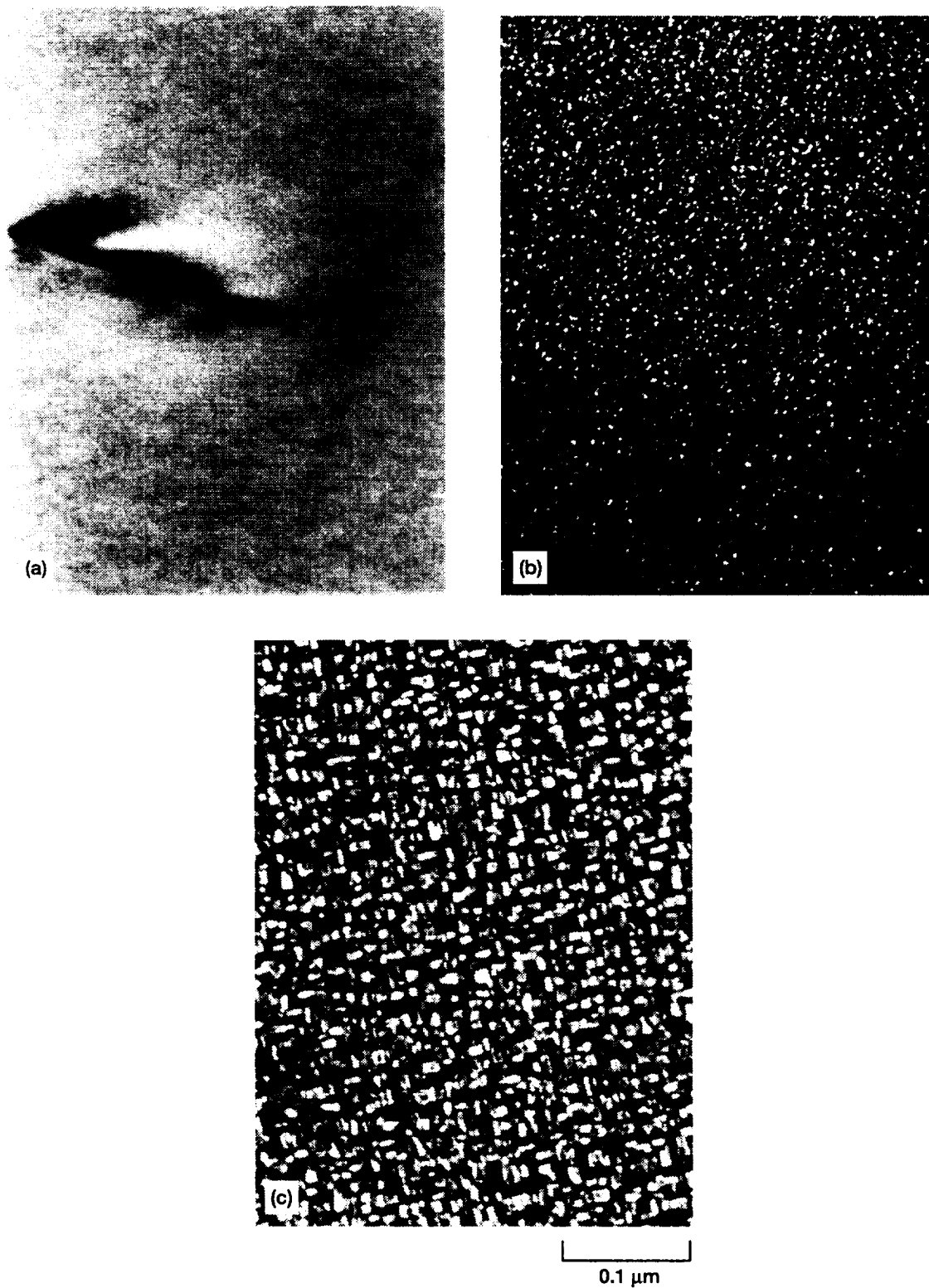


Figure 3.—TEM images of (a) a precipitate-free Ni-47Al-3Ti alloy, (b) precipitation of fine Heusler particles in a Ni-45Al-5Ti alloy and (c) dense precipitation of rectangular shaped Heusler particles in a Ni-43Al-7Ti alloy.

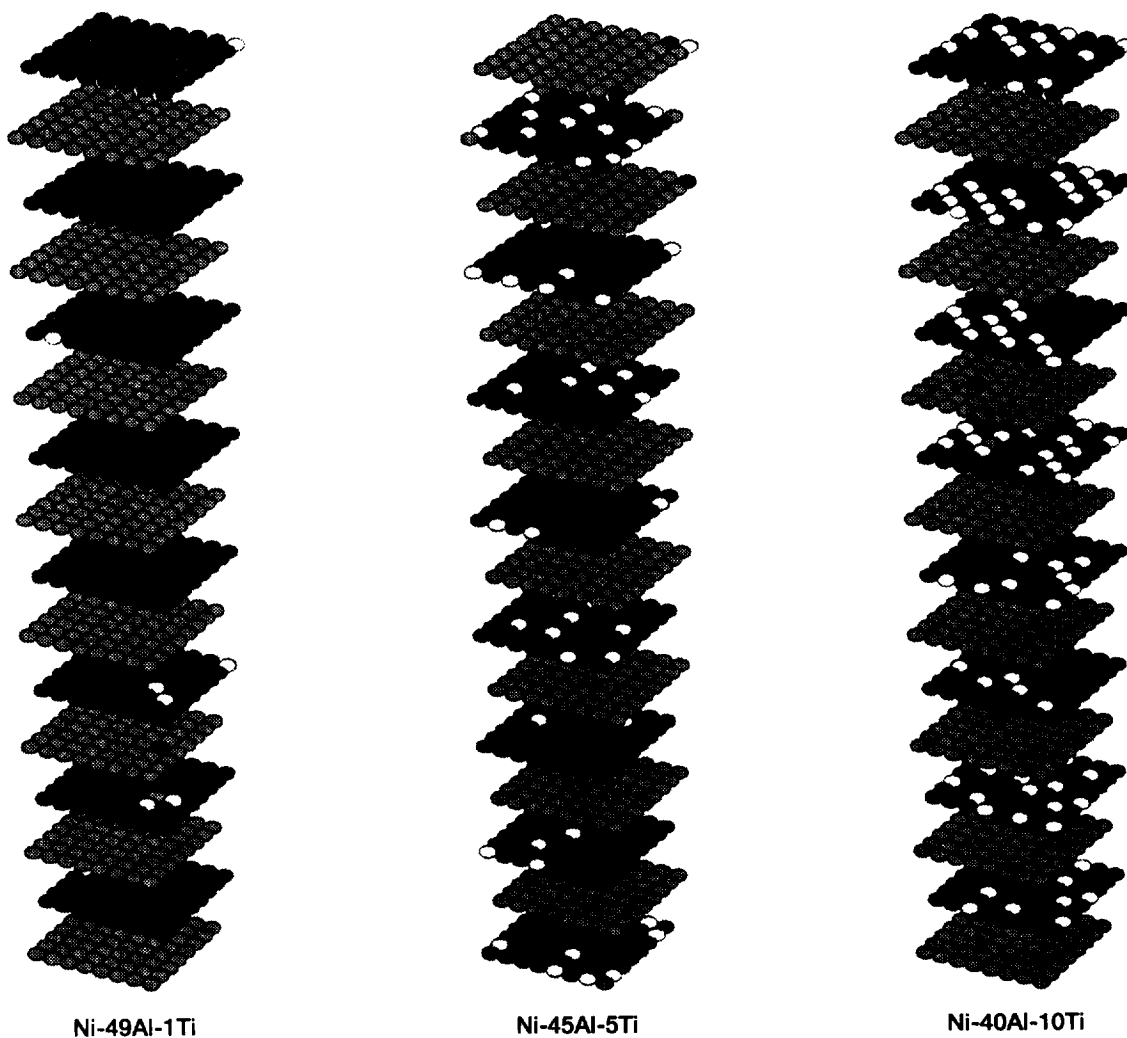


Figure 4.—Final state of temperature-dependent Monte Carlo simulations of initially random 1024-atom cells (a) Ni-49Al-1Ti, (b) Ni-45Al-5Ti and (c) Ni-40Al-10Ti. The Ni, Al and Ti atoms are denoted with black, grey and white spheres respectively. The final state is obtained by lowering the temperature in small steps, starting from a high-temperature, random state.

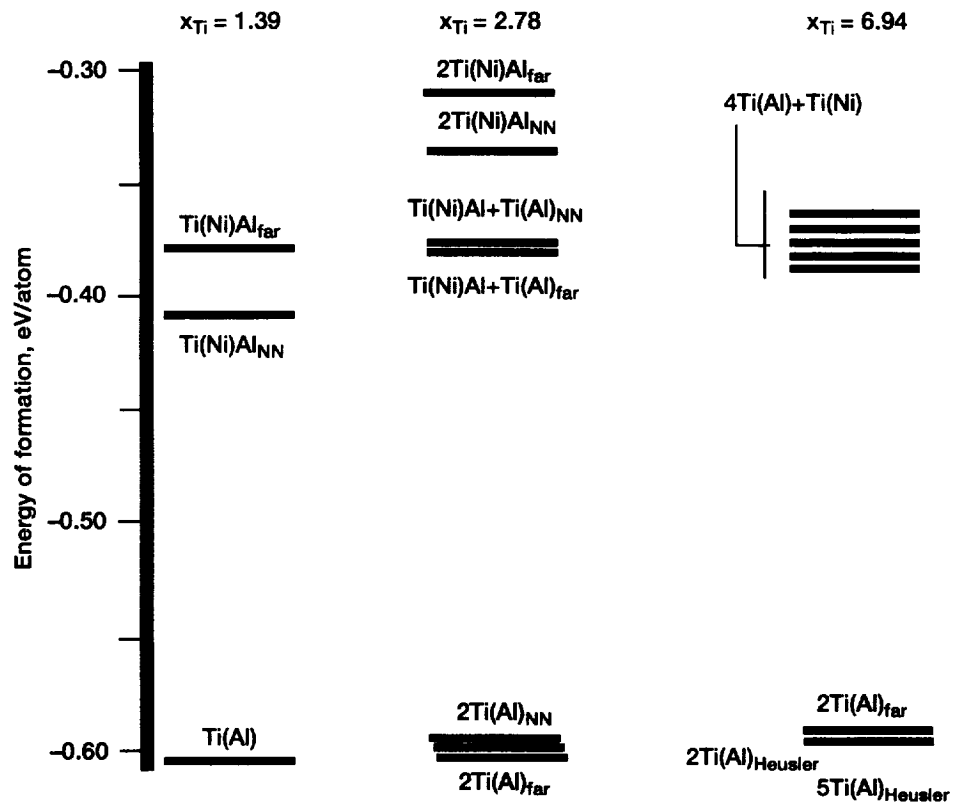


Figure 5.—Site preference energy spectrum for Ni-Al-Ti alloys. A(B) indicates an atom A in a B site and A(B)C indicates an A atom in a B site, with the B atom in a C site. The subindices NN, far and Heusler denote the relative position of the Ti atoms: NN denotes next-nearest neighbor distance, far denotes distances greater than NN and Heusler indicates that the Ti atoms locate themselves in Al site following Heusler ordering.

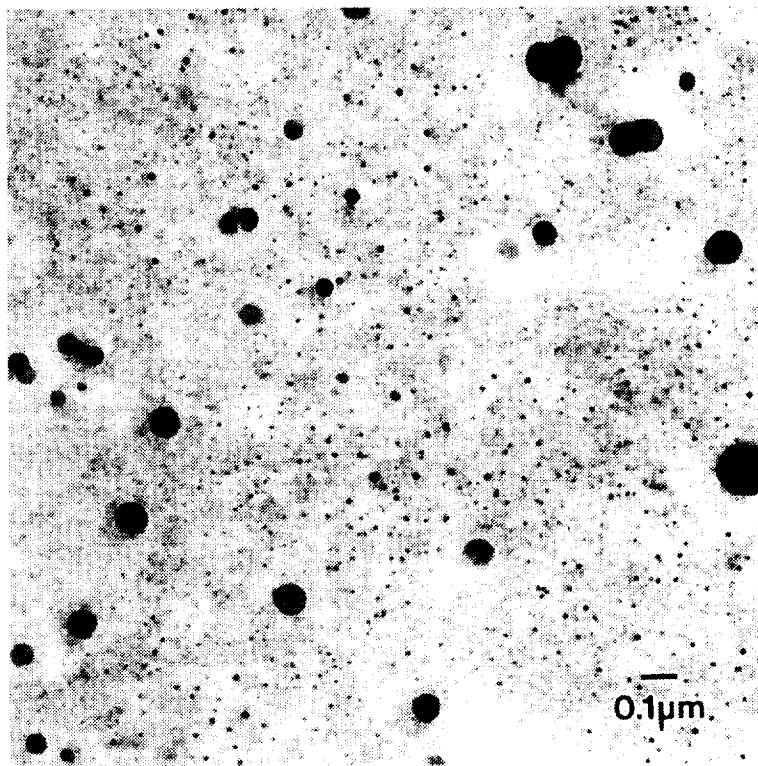
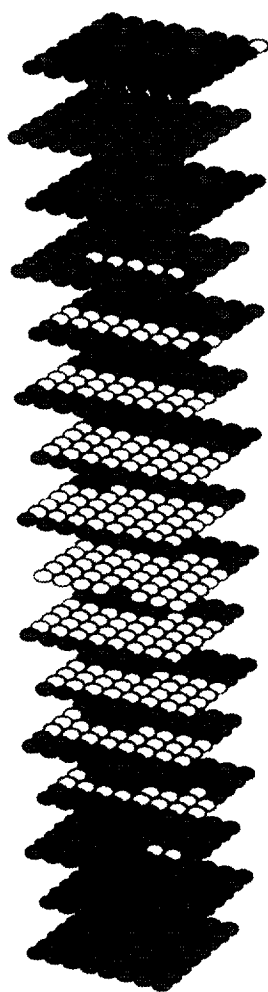
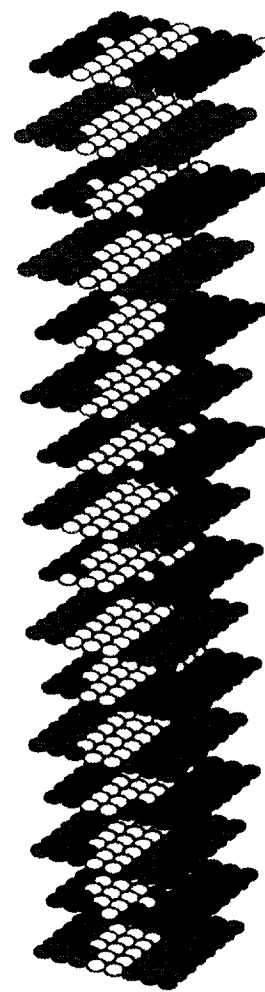


Figure 6.—TEM micrograph of Ni-48Al-2Cr, showing α -Cr precipitates in a β -NiAl matrix.



Ni-25Al-25Cr



Ni-25Al-25Cr

Figure 7.—Final state of Monte Carlo simulations of (a) Ni-25Al-25Cr and (b) Ni 33Al-34Cr. Ni, Al and CR atoms are denoted with black, gray and white spheres respectively.

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